EJTP 3, No. 12 (2006) 47–53 *Electronic Journal of Theoretical Physics*

Light Scattering Studies on the Orientational Behavior of Macromolecular Solutions in a Shear Flow

J.A. Kupriyanova* and A.V. Zatovsky

Department of Theoretical Physics, Odessa National I.I. Mechnikov University, 2 Dvoryanskaya str., 65026 Odessa, Ukraine

Received 19 April 2006, Accepted 20 July 2006, Published 20 September 2006

Abstract: Theoretical investigation of Rayleigh light scattering by a suspension of anisotropic ellipsoidal particles subjected to a shear flow is carried out. Some properties of the suspension of such particles caused by Brownian rotation of these particles are studied. It is shown that the action of a shear flow induces deformations in the shape of scattering line and results into the non-monotonic frequency dependence of depolarized scattering spectral lines with additional local maxima in the spectra.

This work is being dedicated to the memory of Alexandr V. Zatovsky who passed away on August 18, 2006. His field of interest was on the Dynamic Properties of Complex Fluids and Disperse Systems.

Keywords: Shear flow, correlation functions, Brownian motion, light scattering.
PACS (2006): 61.25.Hq; 47.15Gf; 05.40+j, 47.15.gp

1. Introduction

The intensity, polarization and spectral distribution of the scattered light convey significant information about processes that occur in the liquid. Further information on the processes can be obtained by studying the liquid which is subjected to different fields controllable under laboratory conditions. Such fields cause splittings, shifts and spectrum line deformations to appear. The applying of external fields changes the feature of Brownian motion and provides control over the changes in experimental spectra. We investigate theoretically Rayleigh light scattering by a suspension of anisotropic ellipsoidal particles placed into a laminar flow of constant velocity gradient. Such systems can be

* j_kupriyanova@rambler.ru

used to model macromolecular solutions, solutions of anisotropic bacteria or colloidal particles. There are various experimental data showing the shear flow influence on the dynamic characteristics of liquids or the admixtures in liquids [1-3]. The wing of the Rayleigh scattering line by dilute solutions of anisotropic particles can be ascribed to rotational motion of the particles. The changes in scattering spectra are caused by the orientation of the particles in a shear flow. In order to describe the spectroscopy study results, the knowledge of the time correlation functions (CF) for the spherical harmonics of the Euler angles, determining the orientation of the molecule's own reference frame with respect to the laboratory one, is necessary:

$$\Psi_{MK}^{(2)}(t) = \left\langle D_{MK}^{(2)}(t) D_{MK}^{(2)^*}(0) \right\rangle \qquad (1)$$

If the shape of a large macromolecule is approximated, for example, with an ellipsoid, then in the case of equilibrium liquids, these correlations functions are known from a well-developed theory of rotational Brownian motion [4]. But in the case of even simplest Couette flows in liquids, the study CF (1) becomes a very difficult task. Macromolecules in a shear flow are in rotation motion, which leads to significant changes in the scattering spectra [1-3].

2. Analysis

Let the shape of an impurity particle is represented by an ellipsoid. Any change in the orientation of such a particle is only due to its rotation, i. e. its angular velocity. The latter can be represented as a sum of two terms. One is the regular contribution caused by the orienting action of the heterogeneous shear flow, and the other is the random contribution caused by the disorientation Brownian motion of the particle. We restrict ourselves to the case of a flow with a single velocity component $V_x = \Gamma y$. The regular component of the ellipsoid's angular velocity in the ellipsoid's own reference frame then has the Cartesian components [5, 6]

$$\vec{\Omega}^0 = \frac{1}{2}\Gamma\left(\lambda n_1 n_2,\ -\lambda n_2 n_3,\ 1 + \lambda\left(n_2^2 - n_1^2\right)\right), \quad \lambda = \left(b_{||}^2 - b_\perp^2\right) / \left(b_{||}^2 + b_\perp^2\right), \qquad (2)$$

where (n_1, n_2, n_3) - are the unit vectors in this frame along the principal axes of inertia of the ellipsoid, and the parameter λ characterizes the anisotropy of the particle with semi-axes $b_{||}, b_\perp$. Using the complex spherical components of the angular velocity vector, we can represent its components through the Vigner functions of the Euler angles:

$$\Omega_\mu^0 = \frac{\Gamma}{2}\delta_{\mu 0} + \sum_{\alpha=-2}^{2} a_{\mu\alpha} D_{\alpha 0}^{(2)},\ \mu = -1,\ 0,\ 1\ . \qquad (3)$$

Here, the matrix is

$$a_{\mu\alpha} = -\frac{\lambda\Gamma}{2\sqrt{3}}\begin{pmatrix} 0 & 1 & 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 & 1 & 0 \end{pmatrix}.$$

As an external field that determines the heterogeneous conditions in which the impurity macromolecules move, we can choose a constant electric field. In this case, the nonpolar macromolecules are caused by the field to gain an angular momentum, and the regular part of the angular velocity has the components [5]

$$\vec{\Omega} = \left(-\sigma E^2 n_2 n_3,\ \sigma E^2 n_1 n_3\,,\ 0\right).$$

The coefficient σ bears the information of the geometrical parameters of the macromolecules, the polarizability anisotropy, and the properties of the surroundings. A detailed study of the orientation motion of the ellipsoid with an induced dipole moment in an external electric field was initiated by one of us in [7, 8]. Here we take advantage of those results to analyze the orientation motion of the impurity macromolecules in a Couette flow.

We proceed from Langevin's equations, describing the changes in the Vigner functions for the ellipsoid's orientation variables caused by its rotation with constant angular velocity [9]

$$\frac{d}{dt} D^{(l)}_{MK}(t) = -i \sum_{\lambda,\rho} \left[\Omega^0_\lambda(t) + \Omega^r_\lambda(t)\right] D^{(l)}_{M\rho}(t)\ \langle l\rho\,|I_\lambda|\,lK\rangle\,. \tag{4}$$

Here $\Omega^0_\lambda(t)$ and $\Omega^r_\lambda(t)$ are respectively the components of the regular and random components of the angular velocity in a moving reference frame tied up to the object , and $\langle \ldots |I| \ldots \rangle$ are the matrix elements of the projection of the rotation operator on the coordinate axes of the molecular frame in units of h.

Using the method and approach of works [4, 7] and the properties of the matrix elements of the rotation operator, we can find an integro-differential equation for CF (1) of impurity axisymmetric particles in a liquid with a shear flow:

$$\begin{aligned} \tfrac{d}{dt}\Psi^{(l)}_{MK}(t) = &-\tfrac{l(l+1)-K^2}{3\tau^2_\Gamma}\int\limits_0^t dt'\Psi^{(2)}_{10}(t-t')\Psi^{(l)}_{MK}(t') - (\delta_{1,M}+\delta_{-1,M})\delta_{2,l}\delta_{0,K}\tfrac{l(l+1)-K^2}{6\tau^2_\Gamma} \\ &\times\left[\int\limits_0^t dt'\Psi^{(l)}_{10}(t-t')\Psi^{(l)}_{1K}(t') - t\Psi^{(l)}_{1K}(t)\Psi^{(l)}_{1K}(0)\right] - \tfrac{1}{\tau_{lK}}\Psi^{(l)}_{MK}(t), \end{aligned} \tag{5}$$

The expressions for the characteristic time τ_Γ of the orientation change in a shear flow and the relaxation time τ_{lK} of the particle's orientation due to the thermal motion of the particle are of the form

$$\frac{1}{\tau_\Gamma} = \frac{|\lambda|\ \Gamma}{2\sqrt{3}}, \quad \frac{1}{\tau_{lK}} = l(l+1)\Theta_1 + K^2(\Theta_3 - \Theta_1). \tag{6}$$

Here, Θ_i are the principal values of the rotational diffusion tensor.

Note that equation (5) is obtained under assumption $\tau_\Omega << \tau_{lK}$, where τ_Ω is the characteristic time of the angular velocity relaxation. This assumption allows us to consider (4) as a stochastic differential equation with quickly changing disturbance $\Omega^r_\lambda(t)$, so that equation (5) for CF (1) is correct in the first order in magnitude in the small parameter τ_Ω/τ_{lK}.

Hereinafter, we limit the study to the spectral characteristics of CF with the indices $l = 2$,$K = 0$ and $M = 0, \pm 1, \pm 2$. The solution of the integro-differential equation is convenient to search with use of the unilateral Fourier transform for CF:

$$\tilde{\Psi}^{(l)}_{MK}(\omega) = \int\limits_0^\infty dt \Psi^{(l)}_{MK}(t) \exp(i\omega t). \tag{7}$$

In this case, for the CF spectra$\tilde{\Psi}^{(2)}_{00}(\omega)$, $\tilde{\Psi}^{(2)}_{10}(\omega)$ $\tilde{\Psi}^{(2)}_{20}(\omega)$ we have the following closed system of equations

$$\frac{\Psi^{(2)}_{10}(0)}{\tau_\Gamma^2}\frac{\partial \tilde{\Psi}^{(2)}_{10}(\omega)}{\partial(i\omega)} + \left(-i\omega + \frac{1}{\tau_{20}}\right)\tilde{\Psi}^{(2)}_{10}(\omega) + \frac{3}{\tau_\Gamma^2}\left[\tilde{\Psi}^{(2)}_{10}(\omega)\right]^2 = \Psi^{(2)}_{10}(0). \tag{8}$$

$$\tilde{\Psi}^{(2)}_{00}(\omega) = \frac{\Psi^{(2)}_{00}(0)}{-i\omega + \frac{1}{\tau_{20}} + \frac{2}{\tau_\Gamma^2}\tilde{\Psi}^{(2)}_{10}(\omega)}, \quad \tilde{\Psi}^{(2)}_{20}(\omega) = \frac{\Psi^{(2)}_{20}(0)}{-i\omega + \frac{1}{\tau_{20}} + \frac{2}{\tau_\Gamma^2}\tilde{\Psi}^{(2)}_{10}(\omega)} \tag{9}$$

The solution of this system reduces to the integration of nonlinear differential first-order equation (8). The latter can be integrated numerically or analytically. Let us introduce the following unitless quantities values

$$x = \left(-i\omega + \tfrac{1}{\tau_{20}}\right)\frac{\tau_\Gamma}{\sqrt{\Psi^{(2)}_{10}(0)}} = a\ (-i\omega\tau_{20} + 1)\,, \ \ z(x) = -\frac{3}{\tau_\Gamma\sqrt{\Psi^{(2)}_{10}(0)}}\tilde{\Psi}^{(2)}_{10}(\omega), \tag{10}$$

where a is a unitless parameter depending of the velocity gradient of the shear flow:

$$a^{-2} = (\ \tau_{20}/\tau_\Gamma)^2\, \Psi^{(2)}_{10}(0). \tag{11}$$

In the variables x and $z(x)$, differential equation (8) is a special case of the Riccati equation

$$\frac{d}{dx}z(x) + z^2(x) = xz(x) + 3 \tag{12}$$

with additional condition

$$z(0) = -\frac{3}{\tau_E\sqrt{\Psi^{(2)}_{10}(0)}}\int\limits_0^\infty dt \Psi^{(2)}_{10}(t) = -\frac{3}{\sqrt{\Psi^{(2)}_{10}(0)}}\frac{\tau_\vartheta}{\tau_E}. \tag{13}$$

Here $\tau_\vartheta(\Gamma \neq 0)$ is the relaxation time for the CF of the orientation variables $\Psi^{(2)}_{10}(t)$. The solution of the Riccati equation (8) is expressed through algebraic functions and a definite integral (which reduces the error integral by integration by parts; we omit the integration result because of its awkwardness)

$$z(x) = x + \frac{2x}{1+x^2} + \frac{1}{(1+x^2)^2 A(x)}\ ,$$

$$A(x) = \int_0^1 du \left[\frac{xe^{\frac{1}{2}x^2(1-u^2)}}{(1+x^2u^2)^2} - \frac{ae^{\frac{1}{2}(x^2-a^2u^2)}}{(1+a^2u^2)^2} \right] + \frac{e^{\frac{1}{2}(x^2-a^2)}}{(1+a^2)^2} \left[z(0) - a - \frac{2a}{1+a^2} \right]^{-1} . \quad (14)$$

It follows from here and from equation (8) that the function $z(\omega)$ is not monotone. It has a maximum at the frequency value ω_e determined from the relation

$$2Rez(\omega_e) = a - 2Re\left(a^2(1 + i\omega_e\tau_{20})^2 + 4\right)^{1/2} . \quad (15)$$

A non-vanishing solution of (15) occurs if the condition $\tau_\vartheta > 2\tau_{20}/(1 + \sqrt{1 + 12a^{-2}})$ is met. Thus, the spectral density of CF for the orientation variables of the ellipsoid in a shear flow is in general of non-Lorenz form and can have a local maximum that strongly depend on the velocity gradient of the flow.

The complete analysis of the obtained solution of (14) is difficult because of its awkwardness. For the sake of convenience, we calculated the CF spectra by numerical integrating of the equation system (8) for the real and imaginary parts in unitless variables $\tilde{\omega} = \omega\tau_{20}$, $\Psi' + i\Psi'' = \tilde{\Psi}_{00}^{(2)}/\tau_{20}$ taking the initial conditions importance's $\Psi' = \tau_\vartheta(\Gamma \neq 0)/\tau_{20}(\Gamma = 0) \approx 1$, $\Psi''(0) = 0$.

The relaxation times for the orientation motion in absence of the flow and in its presence are not identical, but their explicit dependences of remained undetermined. The figure represents the dependence of the real part of the spectra of $\Psi_{00}^{(2)}$ on the unitless frequency for different values of the shear flow gradient squared $G = a^{-2} \propto \Gamma^2$.

At the presence of a shear flow the contour of a wing of a Rayleigh line is essentially not Lorentzian and can have one or several local maxima. Both shape of a spectrum and peak intensity of these additional maxima varies with an alternation of parameter G value. A position of maxima on the frequencies axis in a short-wave portion of the spectrum also is moved when parameter G increases.

3. Conclusions

Our method makes possible to receive spectra of a Rayleigh light scattering by weak solutions of ellipsoidal particles placed in a shear flow. The presence of a shear flow changes the nature of ellipsoids Brownian rotation that has had an effect on the shape and spectral content of scattered lines. In particular, the contour of a Rayleigh scattering line wing is not Lorentzian and has a fine structure with local maxima. A position on frequencies axis and peak intensity of these additional maxima in Rayleigh scattered line depends both on a shear flow value and the particles sizes. This fact enables to estimate the fragments sizes on changes of light scattering spectra if a shear flow presence.

References

[1] Y. Doppke, W. Heller, J. Phys. Chem. 83 (1989) 1717.

[2] A. V. Lomakin, V. A. Noskin, Lett. JETP 28 (1978) 592.

[3] D. Rusu, P. Van Puyvelde, E. Peuvrel-Disdier, Polymer 40 (1999) 1353.

[4] K. A. Valiev, E. N. Ivanov, UFN 109 (1973) 31.

[5] A.Peterlin, H.A. Stuart, Zeitschrift für Physik 112 (1938) 129.

[6] E. Hinch, L. Leal, J. Fluid Mech. 76 (1976) 187.

[7] A. V. Kyrylyuk, A.V. Zatovsky, Ukr. J. Phys. 49 (2004) 570.

[8] A. V. Kyrylyuk, A.V. Zatovsky, J. Mol. Liq. 120 (2005) 55.

[9] A. S. Davydov, Excited States of Atomic Nuclei, Atomizdat, Moscow, 1967.

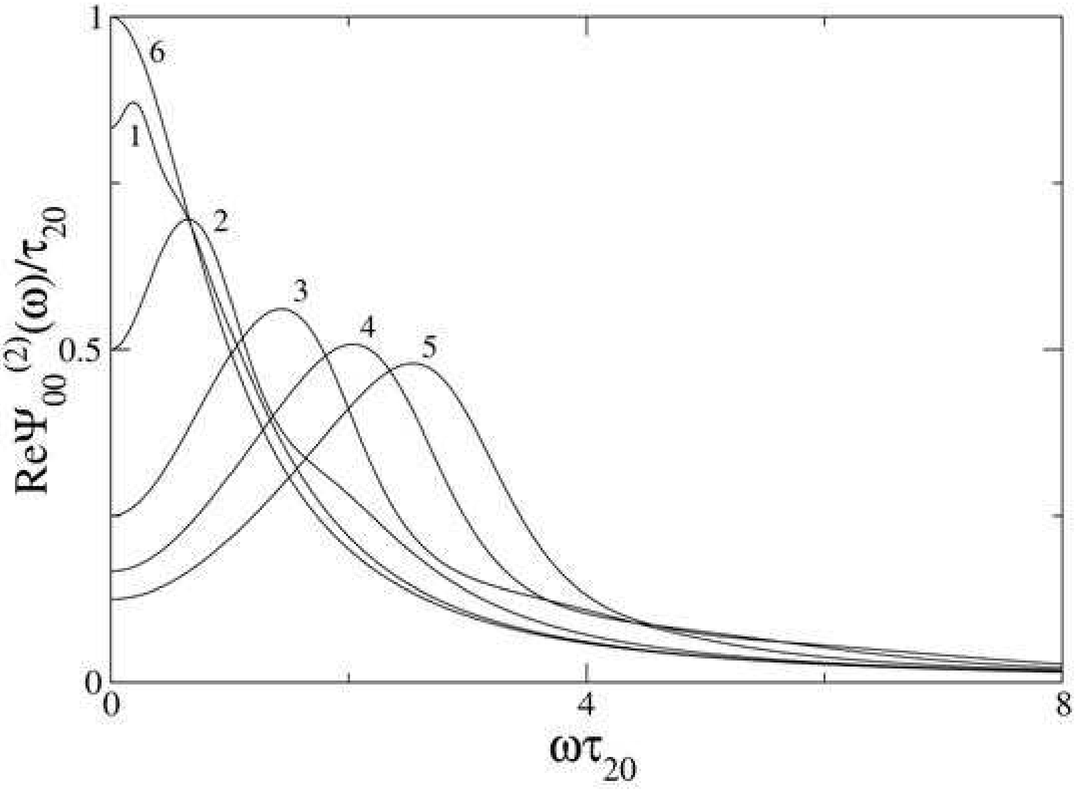

Fig. 1 The spectra of the real part of the correlation function $\Psi_{00}^{(2)}(\omega)/\tau_{20}$ versus the unitless frequency $\tilde{\omega} = \omega\tau_{20}$ for different values of the flow velocity gradient (1 - G=0.1, 2 - 0.5, 3 - 1.5, 4 - 2.5, 5 - 3.5) and in the absence of the flow(6 - G=0).